

## CLAISEN REARRANGEMENT OF 2'-HYDROXY-4-METHOXY-4'-PRENYLOXYCHALCONE

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Claisen rearrangement of 2'-hydroxy-4-methoxy-4'-prenyloxychalcone (II) using acetic anhydride in dimethylaniline gave five compounds and several other minor fractions. The five compounds isolated were *viz.* 2'-hydroxy-4-methoxy-4',4',5"-trimethyldihydro furano (2",3":4',3') chalcone (III), 2'-hydroxy-4'-acetoxy-4-methoxy-3'-( $\alpha,\alpha$ -dimethylallyl)chalcone (IV), 2'-hydroxy-4'-acetoxy-4-methoxy-5'-( $\alpha,\alpha$ -dimethylallyl)chalcone (V), 2'-acetoxy-4-methoxy-4'-prenyloxychalcone (VI) and 2'-hydroxy-4'-acetoxy-4-methoxy chalcone (VII). Mild alkaline hydrolysis of IV gave 2',4'-dihydroxy-4-methoxy-3'-( $\alpha,\alpha$ -dimethylallyl) chalcone (VIII). The products have been characterized by their spectral analysis.

**Key words:** Claisen rearrangement, Chalcone and derivatives.

### Introduction

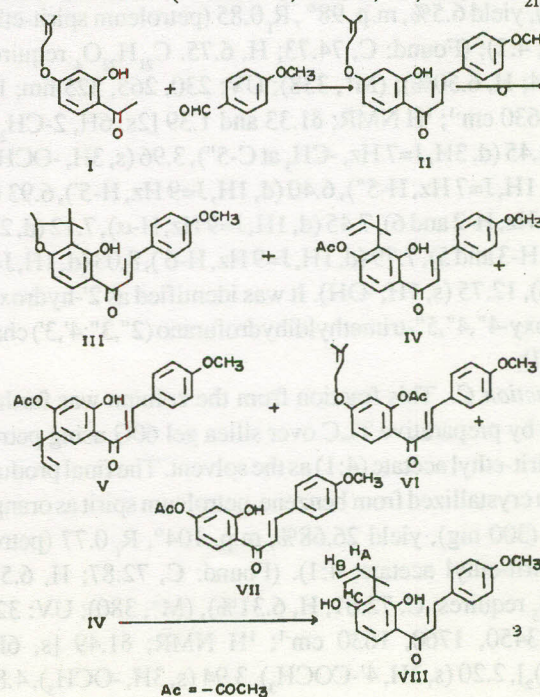
Although much work has been reported on the Claisen rearrangement of 3-methyl-2-butenyl ether of xanthenes [1], coumarins [2,3] and related compounds [4], such studies on flavonoids appeared to have received little attention. Recently Jain *et al.* [5,6] and Islam *et al.* [7] carried out the Claisen rearrangement of flavones, chalcones and related compounds. Though the formation of abnormal rearrangement products is reported in other system [1-3] no such products are formed from flavonoids. The chalcone (II) used for the Claisen rearrangement was obtained by the condensation of 2-hydroxy-4-prenyloxyacetophenone [8] (I) with anisaldehyde under alkaline condition.  $\beta$ -Resacetophenone when refluxed with prenyl bromide [9] in presence of  $K_2CO_3$  in acetone gave 2-hydroxy-4-prenyloxyacetophenone [8] (I). Results are reported of the Claisen rearrangement of chalcone (II) with  $Ac_2O$  in dimethylaniline and the mild alkaline hydrolysis of one of the isolated products IV (Scheme 1). The isolation of the major products by chromatographic technique and the characterization of the products are also reported.

### Experimental

Melting points were determined on Gallenkamp and are uncorrected. IR spectra were recorded on KBr discs on a Pye-Unicam SP3-300 IR spectrophotometer.  $^1H$  NMR spectra were recorded on a Perkin-Elmer R-32 (90 MHz) spectrophotometer in  $CDCl_3$  with TMS as an internal standard (the chemical shifts are given in  $\delta$  values). UV spectra ( $\lambda_{max}$  in nm) were recorded on Beckman DU-2 spectrophotometer Ultrospeck in methanol. TLC was performed with silica gel 60G. Satisfactory elemental analysis were obtained for all the compounds and structures are in accord with the UV, IR and  $^1H$  NMR data. Mass spectra were recorded on VG 7070 E

analytical mass spectrometer.

**2'-Hydroxy-4-methoxy-4'-prenyloxychalcone (II).** Aq. potassium hydroxide (2.8 g/2.8 ml  $H_2O$ ) was added to a solution of 2-hydroxy-4-prenyloxyacetophenone [8] (I, 2.5 g) and anisaldehyde (1.65 g) in ethanol (30 ml). The solution was kept at room temperature for 48 hrs. Diluted with ice cold water and acidified with cold dil. HCl. The solid product was filtered and was washed with petroleum spirit and 5%  $NaHCO_3$  solution. It was crystallized from ethanol as yellow needles (2.35 g), yield 61.18%, m.p.  $96^\circ$ ,  $R_f$  0.78 (petroleum spirit-ethyl acetate; 4:1). It gave brown colour with alcoholic ferric chloride solution. (Found: C, 74.79; H, 6.63.  $C_{21}H_{22}O_4$



Scheme 1.

requires: C, 74.55; H, 6.51%); ( $M^+$ , 338); UV: 225, 250, 325 nm; IR: 3450, 1630  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$ 1.75 [s, 6H,  $>\text{C}(\text{CH}_3)_2$ ], 3.92 (s, 3H,  $-\text{OCH}_3$ ), 4.53 (d, 2H,  $J=7$  Hz,  $-\text{O}-\text{CH}_2-\text{CH}=\text{}$ ), 5.44 (t, 1H,  $J=7$  Hz,  $-\text{O}-\text{CH}_2-\text{CH}=\text{}$ ), 6.23 (s, 1H, H-3'), 6.42 (d, 1H,  $J=9$  Hz, H-5'), 6.92 (d, 2H,  $J=9$  Hz, H-2 and 6), 7.45 (d, 1H,  $J=9$  Hz, H- $\alpha$ ), 7.58 (d, 2H,  $J=9$  Hz, H-3 and 5), 7.93-8.03 (m, 2H, H- $\beta$  and 6').

*Claisen rearrangement of 2'-hydroxy-4-methoxy-4'-prenyloxychalcone (II).* Oxygen free  $\text{N}_2$  was passed through a solution of the chalcone (II, 1g) in freshly distilled  $\text{N,N}$ -dimethylaniline (10 ml) and acetic anhydride (1 ml) contained in a heavy walled glass tube. The tube was carefully sealed and immersed in an oil bath at  $185 \pm 5^\circ$  and kept at this temperature for 4 hrs. The mixture was diluted with ice cold water (150 ml), set aside for 2 hrs and extracted with ethyl acetate. The ethyl acetate layer was treated with dil. HCl (1%, w/v) to obtain a solution of pH 2 followed by aq.  $\text{K}_2\text{CO}_3$  (5%, w/v) to pH 11 and finally with brine to neutrality. The organic layer was dried and evaporated to a crude mass. Fractionation of the crude mass over silica gel 60G using petroleum spirit, petroleum spirit-benzene (2:1), benzene-petroleum spirit (3:2) and increasing quantities of benzene as eluents gave the following major fractions (A-F).

*Fraction A.* Crystallization from benzene-petroleum spirit afforded the starting chalcone (II, 75 mg), yield 7.5%, m.p.  $96^\circ$ .

*Fraction B.* Purification by preparative TLC over silica gel 60G using petroleum spirit-ethyl acetate (4:1) as the solvent was undertaken. The product obtained was then crystallized from benzene-petroleum spirit as yellow needles (65 mg), yield 6.5%, m.p.  $98^\circ$ ,  $R_f$  0.85 (petroleum spirit-ethyl acetate; 4:1); (Found: C, 74.73; H, 6.75.  $\text{C}_{21}\text{H}_{22}\text{O}_4$  requires: C, 74.54; H, 6.50%); ( $M^+$ , 338); UV: 230, 265, 325 nm; IR: 3440, 1630  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$ 1.33 and 1.39 [2s, 6H, 2- $\text{CH}_3$  at C-4"], 1.45 (d, 3H,  $J=7$  Hz,  $-\text{CH}_3$  at C-5"), 3.96 (s, 3H,  $-\text{OCH}_3$ ), 4.47 (q, 1H,  $J=7$  Hz, H-5"), 6.40 (d, 1H,  $J=9$  Hz, H-5'), 6.93 (d, 2H,  $J=9$  Hz, H-2 and 6), 7.45 (d, 1H,  $J=9$  Hz, H- $\alpha$ ), 7.12 (d, 2H,  $J=9$  Hz, H-3 and 5), 7.79 (d, 1H,  $J=9$  Hz, H-6'), 8.03 (d, 1H,  $J=9$  Hz, H- $\beta$ ), 12.75 (s, 1H,  $-\text{OH}$ ). It was identified as 2'-hydroxy-4-methoxy-4",4",5"-trimethyldihydrofurano(2",3":4',3') chalcone (III).

*Fraction C.* This fraction from the column was further purified by preparative TLC over silica gel 60G using petroleum spirit-ethyl acetate (4:1) as the solvent. The final product was then crystallized from benzene-petroleum spirit as orange needles (300 mg), yield 26.68%, m.p.  $104^\circ$ ,  $R_f$  0.77 (petroleum spirit-ethyl acetate; 4:1). (Found: C, 72.87; H, 6.55.  $\text{C}_{23}\text{H}_{24}\text{O}_5$  requires: C, 72.61; H, 6.31%); ( $M^+$ , 380); UV: 325 nm; IR: 3450, 1760, 1630  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$ 1.49 [s, 6H,  $>\text{C}(\text{CH}_3)_2$ ], 2.20 (s, 3H, 4'- $\text{COCH}_3$ ), 3.94 (s, 3H,  $-\text{OCH}_3$ ), 4.81

(dd, 2H,  $J=10$  and 18 Hz,  $\text{H}_\beta$  and  $\text{H}_\gamma$ ), 6.24 (dd, 1H,  $J=10$  and 18 Hz,  $\text{H}_\alpha$ ), 6.42 (d, 1H,  $J=9$  Hz, H-5'), 6.89 (d, 2H,  $J=9$  Hz, H-2 and 6), 7.45 (d, 1H,  $J=9$  Hz, H- $\alpha$ ), 7.58 (d, 2H,  $J=9$  Hz, H-3 and 5), 7.78 (d, 1H,  $J=9$  Hz, H-6'), 8.03 (d, 1H,  $J=9$  Hz, H- $\beta$ ), 12.65 (s, 1H,  $-\text{OH}$ ). It was identified as 2'-hydroxy-4'-acetoxy-4-methoxy-3'-( $\alpha,\alpha$ -dimethyl-allyl) chalcone (IV).

*Fraction D.* Crystallization from benzene-petroleum spirit yielded yellow needles (65 mg), yield 5.78%, m.p.  $101^\circ$ ,  $R_f$  0.63 (petroleum spirit-ethyl acetate; 4:1). (Found: C, 72.93; H, 6.53.  $\text{C}_{23}\text{H}_{24}\text{O}_5$  requires: C, 72.62; H, 6.33%); ( $M^+$ , 380); UV: 225, 325 nm; IR: 3445, 1760, 1640  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$ 1.42 [s, 6H,  $>\text{C}(\text{CH}_3)_2$ ], 2.22 (s, 3H, 4'- $\text{COCH}_3$ ), 3.95 (s, 3H,  $-\text{OCH}_3$ ), 4.94 (dd, 2H,  $J=10$  and 18 Hz,  $\text{H}_\beta$  and  $\text{H}_\gamma$ ), 6.20 (dd, 1H,  $J=10$  and 18 Hz,  $\text{H}_\alpha$ ), 6.49 (s, 1H, H-3'), 6.90 (d, 2H,  $J=9$  Hz, H-2 and 6), 7.41 (d, 1H,  $J=9$  Hz, H- $\alpha$ ), 7.53 (d, 2H,  $J=9$  Hz, H-3 and 5), 7.84 (s, 1H, H-6'), 8.01 (d, 1H,  $J=9$  Hz, H- $\beta$ ), 13.01 (s, 1H,  $-\text{OH}$ ). It was identified as 2'-hydroxy-4'-acetoxy-4-methoxy-5'-( $\alpha,\alpha$ -dimethylallyl) chalcone (V).

*Fraction E.* This fraction from the column was purified by preparative TLC over silica gel 60G using petroleum spirit-ethyl acetate (4:1) as the solvent. The final product was crystallized from benzene-petroleum spirit as pale yellow crystals (275 mg), yield 24.46%, m.p.  $79-80^\circ$ ,  $R_f$  0.49 (petroleum spirit-ethyl acetate; 4:1), (Found: C, 72.93; H, 6.52.  $\text{C}_{23}\text{H}_{24}\text{O}_5$  requires: C, 72.64; H, 6.31%); ( $M^+$ , 380); UV: 225, 255, 320 nm; IR: 1765, 1638  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$ 1.73 [s, 6H,  $>\text{C}(\text{CH}_3)_2$ ], 2.24 (s, 3H, 2'- $\text{COCH}_3$ ), 3.94 (s, 3H,  $\text{OCH}_3$ ), 4.53 (d, 2H,  $J=7$  Hz,  $-\text{O}-\text{CH}_2-\text{CH}=\text{}$ ), 5.44 (t, 1H,  $J=7$  Hz,  $-\text{O}-\text{CH}_2-\text{CH}=\text{}$ ), 6.26 (s, 1H, H-3'), 6.44 (d, 1H,  $J=9$  Hz, H-5'), 6.94 (d, 2H,  $J=9$  Hz, H-2 and 6), 7.41 (d, 1H,  $J=9$  Hz, H- $\alpha$ ), 7.56 (d, 2H,  $J=9$  Hz, H-3 and 5), 7.78 (d, 1H,  $J=9$  Hz, H-6'), 8.02 (d, 1H,  $J=9$  Hz, H- $\beta$ ). It was identified as 2'-acetoxy-4-methoxy-4'-prenyloxychalcone (VI).

*Fraction F.* This isolated fraction from the column was further purified by preparative TLC over silica gel 60G using petroleum spirit-ethyl acetate (4:1) as the solvent. The final product was crystallized from ethanol as yellow crystals (80 mg), yield 8.6%,  $R_f$  0.40 (petroleum spirit-ethyl acetate; 4:1); (Found: C, 69.41; H, 5.31.  $\text{C}_{18}\text{H}_{16}\text{O}_5$  requires: C, 69.22; H, 5.12%); ( $M^+$ , 312); UV: 250, 315 nm; IR: 3430, 1762, 1640  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$ 2.30 (s, 3H, 4'- $\text{COCH}_3$ ), 3.96 (s, 3H,  $-\text{OCH}_3$ ), 6.25 (s, 1H, H-3'), 6.46 (d, 1H,  $J=9$  Hz, H-5'), 6.92 (d, 2H,  $J=9$  Hz, H-2 and 6), 7.43 (d, 1H,  $J=9$  Hz, H- $\alpha$ ), 7.59 (d, 2H,  $J=9$  Hz, H-3 and 5), 7.90 (m, 2H, H- $\beta$  and 6'), 13.01 (s, 1H,  $-\text{OH}$ ). It was identified as 2'-hydroxy-4'-acetoxy-4-methoxychalcone (VII).

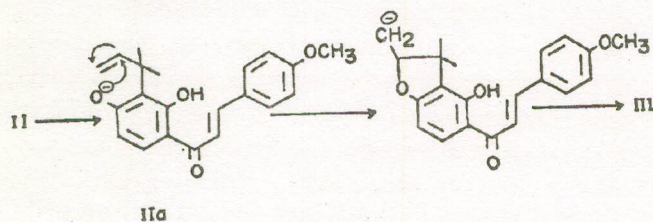
*Hydrolysis of IV to 2', 4'-dihydroxy-4-methoxy-3'-( $\alpha,\alpha$ -dimethylallyl) chalcone (VIII).* The acetate of IV, (250 mg) was dissolved in ethanol (15 ml) with gentle heating. Sodium hydroxide in ethanol (1%, w/v, 5 ml) was added to the solution and the mixture was warmed on steam bath for one minute

until the orange-red colour changed to yellow. The solution was then carefully neutralized with cold dil. HCl (1%, w/v) and extracted with ether. The usual work-up gave a crude product which on separation by preparative T.L.C. over silica gel 60G using petroleum spirit-ethyl acetate (5:1) as the developing solvent. The product was crystallized from benzene-petroleum spirit as yellow crystals (105 mg), yield 47.21%, m.p. 98°,  $R_f$  0.48 (petroleum spirit-ethyl acetate; 5:1). It gave brown colour with alcoholic ferric chloride solution. (Found: C, 74.73; H, 6.78.  $C_{21}H_{22}O_4$  requires: C, 74.54; H, 6.53%); ( $M^+$ , 338); UV: 230, 255, 340 nm; IR: 3450, 1635  $cm^{-1}$ ;  $^1H$  NMR:  $\delta$  1.45 [s, 6H,  $>C(CH_3)_2$ ], 3.95 (s, 3H,  $-OCH_3$ ), 4.86 (dd, 2H,  $J=10$  and 18 Hz,  $H_B$  and  $H_C$ ), 6.24 (dd, 1H,  $J=10$  and 18 Hz,  $H_A$ ), 6.43 (d, 1H,  $J=9$  Hz, H-5'), 6.96 (d, 2H,  $J=9$  Hz, H-2 and 6) 7.44 (d, 1H,  $J=9$  Hz, H- $\alpha$ ), 7.60 (d, 1H,  $J=9$  Hz, H-3 and 5), 7.79 (d, 1H,  $J=9$  Hz, H-6'), 8.01 (d, 1H,  $J=9$  Hz, H- $\beta$ ), 13.25 (s, 1H,  $-OH$ ).

### Results and Discussions

The compound II was subjected to Claisen rearrangement condition and major compounds III, IV, V, VI and VII were isolated from the reaction. The compounds III, IV and V are rearranged products in which cases the allyl group migrated from the phenolic oxygen to adjacent available aromatic ring carbons (C-3' and/or 5'). The compound III was obtained through the cyclization of the presumably rearranged product IIa as shown in Scheme 2.

The preferred formation of 5-membered ring was also



supported by the  $^1H$  NMR spectrum of compound III. A methyl doublet at  $\delta$  1.45 and a methine quartet at  $\delta$  4.47 confirmed the formation of 5-membered ring. The fact that the allyl group has migrated to the C-3' position in these compounds was shown by the two doublets at  $\delta$  6.40 and 7.79 for C-5' and 6' protons respectively. The fact that the 2'-OH group appeared not to be involved in cyclization could be due to it being in the sterically crowded position. Compound IV was produced by the migration of allyl group in compound II to C-3' of the same aromatic ring followed by oxy-acetylation of the rearranged product at C-4' position. The observation has been confirmed by IR and  $^1H$  NMR spectra. IR absorption frequencies of compound IV ( $\nu_{max}$ ) 1760, 1630  $cm^{-1}$  indicated the presence of an ester carbonyl and a conjugated carbonyl

groups respectively.  $^1H$  NMR spectra showed a singlet at  $\delta$  2.20 indicating the presence of the methyl protons of  $-COCH_3$  group. The two doublets at  $\delta$  6.42 and 7.78 may be assigned to C-5' and 6' protons of the aromatic ring.

Compound V is isomeric to compound IV in which allyl group moiety has migrated to C-5' position of the same aromatic ring and oxy-acetylation of the resulting oxy-anion at C-4' has taken place. The IR spectrum of compound V showed absorption frequencies at 1760 and 1640  $cm^{-1}$  indicating the presence of an ester carbonyl and a conjugated carbonyl groups respectively. In  $^1H$  NMR spectrum of compound V two singlets at  $\delta$  6.49 and  $\delta$  7.84 may be assigned to C-3' and C-6' protons of the aromatic ring. In compound VI only an oxy-acylation at C-2' of compound II has taken place. In IR spectrum a new absorption at 1765  $cm^{-1}$  for ester carbonyl group was observed whereas the absorption frequency at 3450  $cm^{-1}$  due to phenolic hydroxyl group disappeared.

In compound VII, deisoprenylation followed by an oxy-acylation at C-4' of compound II has taken place. IR absorption frequencies at 3430, 1762 and 1640  $cm^{-1}$  indicating the presence of phenolic hydroxyl, ester carbonyl and conjugated carbonyl groups respectively.

In compound VIII obtained from compound VI by its hydrolysis with NaOH in ethanol, IR absorption frequency at 1760  $cm^{-1}$  (ester carbonyl) disappeared. In  $^1H$  NMR spectrum the singlet at  $\delta$  2.20 disappeared indicating an acyl-oxygen cleavage at C-4' position.

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Compound V is isomeric to compound IV in which allyl group moiety has migrated to C-2' position of the same aromatic ring and oxy-acetylation of the resulting oxy-anion at C-4' has taken place. The IR spectrum of compound V showed absorption frequencies at 1700 and 1640 cm<sup>-1</sup> indicating the presence of an ester carbonyl and a conjugated carbonyl groups respectively. In <sup>1</sup>H NMR spectrum of compound V two singlets at δ 6.49 and δ 7.84 may be assigned to C-3' and C-6' protons of the aromatic ring. In compound VI only an oxy-acetylation at C-2' of compound II has taken place. In IR spectrum a new absorption at 1705 cm<sup>-1</sup> for ester carbonyl group was observed whereas the absorption frequency at 3450 cm<sup>-1</sup> due to phenolic hydroxyl group disappeared.

In compound VII deacetylation followed by an oxy-acetylation at C-4' of compound II has taken place. IR absorption frequencies at 3430, 1703 and 1640 cm<sup>-1</sup> indicating the presence of phenolic hydroxyl, ester carbonyl and conjugated carbonyl groups respectively.

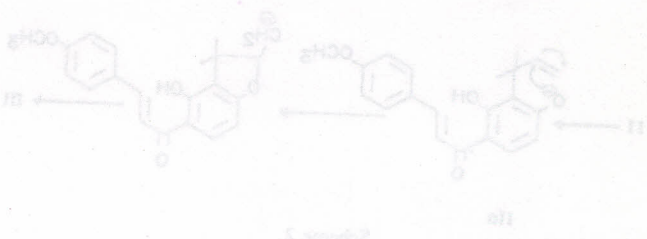
In compound VIII obtained from compound VI by its hydrolysis with NaOH in ethanol, IR absorption frequency at 1700 cm<sup>-1</sup> (ester carbonyl) disappeared. In <sup>1</sup>H NMR spectrum the singlet at δ 7.20 disappeared indicating an acyl-oxygen cleavage at C-4' position.

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The compound II was subjected to Claisen rearrangement condition and major compounds III, IV, V, VI and VII were isolated from the reaction. The compounds III, IV and V are rearranged products in which cases the allyl group migrated from the phenolic oxygen to adjacent available aromatic ring carbons (C-2' and/or 2'). The compound III was obtained through the cyclization of the presumably rearranged product. It is shown in scheme 2.

The proposed formation of 2-membered ring was also supported by the <sup>1</sup>H NMR spectrum of compound III. A methyl doublet at δ 1.45 and a methine quartet at δ 4.47 confirmed the formation of 2-membered ring. The fact that the allyl group has migrated to the C-3' position in these compounds was shown by the two doublets at δ 6.40 and 7.79 for C-2' and 6' protons respectively. The fact that the 2-OH group appeared not to be involved in cyclization could be due to it being in the sterically crowded position. Compound IV was produced by the migration of allyl group in compound II to C-2' of the same aromatic ring followed by oxy-acetylation of the rearranged product at C-4' position. The observation has been confirmed by IR and <sup>1</sup>H NMR spectra. IR absorption frequencies of compound IV (ν<sub>max</sub>) 1700; 1630 cm<sup>-1</sup> indicated the presence of an ester carbonyl and a conjugated carbonyl



Scheme 2

product which on separation by precipitation with 60% ethyl alcohol gave compound III (3:1) as the major product. The product was crystallized from benzene-petroleum spirit as yellow crystals (105 mg), yield 47.21%, m.p. 98°, R<sub>f</sub> 0.48 (petroleum spirit-ethyl acetate); solution (found): C, 74.73; H, 6.78; O, 18.49; mp 98-100°C; IR (KBr): ν<sub>max</sub> 3450, 3300, 3100, 3000, 2900, 2800, 2700, 2600, 2500, 2400, 2300, 2200, 2100, 2000, 1900, 1800, 1700, 1600, 1500, 1400, 1300, 1200, 1100, 1000, 900, 800, 700, 600, 500, 400, 300, 200, 100 cm<sup>-1</sup>; <sup>1</sup>H NMR: δ 1.45 (d, 3H, H<sub>a</sub>), 1.95 (s, 3H, H<sub>b</sub>), 4.85 (dd, 2H, H<sub>c</sub> and H<sub>d</sub>), 6.24 (dd, 1H, H<sub>e</sub> and 1H, H<sub>f</sub>), 6.43 (d, 1H, H<sub>g</sub>), 6.96 (d, 1H, H<sub>h</sub>), 7.44 (d, 1H, H<sub>i</sub>), 7.60 (d, 1H, H<sub>j</sub>), 7.79 (d, 1H, H<sub>k</sub>), 8.01 (d, 1H, H<sub>l</sub>), 12.22 (s, 1H, OH).